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Description

TECHNICAL FIELD

The present invention relates to granular detergent compositions and components of high bulk density, and their preparation by a dry neutralisation process.

BACKGROUND AND PRIOR ART

Recently there has been considerable interest within the detergents industry in the production of detergent powders having relatively high bulk density, for example, 650 g/litre and above. It has been suggested that such powders containing anionic surfactants, for example alkyl benzene sulphonate, may be prepared by methods involving in-situ neutralisation of an acid precursor of the anionic surfactant with an alkali such as sodium hydroxide or sodium carbonate.

For example, JP 60 072 999A (Kao) and GB 2 166 452B (Kao) disclose a process in which detergent sulphonic acid, sodium carbonate and water are mixed in a strongly shearing apparatus; the solid mass obtained is cooled to 40 °C or below and pulverised; and the fine powder thus obtained is granulated. This process is typical of those disclosed in the art in that the product of the neutralisation reaction is a doughy mass, and the reaction requires apparatus such as a kneader with a very high energy requirement; and separate pulverisation and granulation steps in different apparatus are required in order to obtain an acceptable granular detergent product.

There has also been considerable recent interest in the use of high-speed mixer/granulators in the preparation of high-bulk-density detergent powders. For example, EP 158 419B (Hashimura) discloses a process in which nonionic surfactant and soda ash are mixed and granulated in a reactor having horizontal and vertical blades rotating at different speeds, to give a detergent powder built with sodium carbonate and containing a high level of nonionic surfactant.

GB 1 404 317 (Bell) discloses the preparation of a detergent powder of low or moderate bulk density by a dry neutralisation process. Detergent sulphonic acid is mixed with an excess of soda ash in the presence of sufficient water to initiate the neutralisation reaction but not enough to wet the resultant product, which is in the form of a free-flowing powder. The process is carried out in apparatus, for example a ribbon blender, planetary mixer or air transfer mixer, in which the reactants are "tossed and fluffed", and carbon dioxide liberated during the neutralisation is entrapped in the product particles. The process is thus directed towards the production of light, porous particles comparable to those obtained by spray-drying.

GB 1 369 269 (Colgate) discloses a process for the production of anionic detergent, by vigorously mixing detergent sulphonic acid with powdered sodium carbonate in a mixer with a cutting arrangement, for example a Lödige ploughshare mixer. In order to obtain a granular product rather than a doughy mass, it is necessary to blow the detergent sulphonic acid in by means of a gas stream, to ensure adequate fluidisation and mixing of the reactants: this requires quite complex modification of the mixer. No water is added to promote the neutralisation reaction, which therefore proceeds slowly and produces a relatively coarse product requiring an additional size reduction step. The temperature during neutralisation typically rises to about 85 °C.

US 4 690 785 (Witco) discloses a process for the production of alkylbenzene sulphonate powder by the neutralisation of alkylbenzene sulphonic acid with a base in solid or solution form. A substantial amount of water is present at the beginning of the process, and the heat generated by the exothermic reaction is used to drive off this, and the water generated by the reaction itself; reaction temperatures of about 100 °C are typical.

In the seventh edition of "Synthetic Detergents" by Davidsohn and Milwidsky, 1987, pages 202-209 describe the production of detergent compositions by combined absorption and neutralisation. On pages 208 and 209 it is stated that high speed mixers fitted with rotating knives can be used to produce dry neutralised powders in a single step without ageing and grinding. The bulk density of such powders is not stated.

The present inventors have now discovered that free-flowing detergent powders and detergent powder components of high bulk density and small particle size can be produced by dry neutralisation at relatively low temperatures, using only a single piece of apparatus: a high-speed mixer/granulator having both a stirring action and a cutting action.

DEFINITION OF THE INVENTION

The present invention accordingly provides a process for the preparation of a granular detergent composition or component having a bulk density of at least 650 g/litre, which process includes the step of neutralising a liquid acid precursor of an anionic surfactant with a solid water-soluble alkaline inorganic material, the process being characterised by the steps of:

(i) fluidising a particulate solid water-soluble alkaline inorganic material in an amount in excess of that required for neutralisation, optionally in admixture with one or more other particulate solids, in a high-speed mixer/granulator having both a stirring action and a cutting action;

(ii) gradually adding the acid precursor to the high-speed mixer/granulator, while maintaining a temperature not higher than 55°C, whereby neutralisation of the acid precursor by the water-soluble alkaline inorganic material occurs while the mixture remains in particulate form;

(iii) granulating the mixture in the high-speed mixer/granulator, in the presence of a liquid binder,

whereby a granular detergent composition or component having a bulk density of at least 650 g/litre is formed.

The invention also provides a granular detergent composition or component prepared by this process.

DETAILED DESCRIPTION OF THE INVENTION

The process

DETAILED DESCRIPTION OF THE INVENTION

The subject of the invention is the preparation of high-bulk-density detergent powder by a process involving the dry neutralisation of the acid precursor of an anionic surfactant with an alkaline solid. The process is carried out in a high-speed mixer/granulator and involves the previously defined process steps (i), (ii) and (iii).

A very important characteristic of the process of the invention is that the reaction mixture remains throughout in particulate or granular form. Caking, balling and dough formation are avoided, and the product at the end of the granulation step needs no further particle size reduction. The process of the invention generally produces a granular product containing at least 50 wt%, preferably at least 70 wt%, of particles smaller than 1700 µm. This is achieved by ensuring that liquid components, particularly the acid anionic surfactant precursor, do not have an opportunity to act as binders or agglomerating agents.

First, step (i) ensures that there is initially a large amount of particulate solids present, relative to the liquids to be added, in the mixer before the introduction of the liquids. Preferably the total solids present in step (i) amount to at least 60 wt%, more preferably at least 67 wt%, of the total composition present in step (ii). It is therefore advantageous to add as high a proportion as possible of the solid ingredients of the final product at this stage. Preferably the liquids to solids ratio at the end of the neutralisation step (ii) does not exceed 0.60; more preferably it does not exceed 0.55, and desirably it does not exceed 0.50.

The solids must of course include a particulate water-soluble alkaline inorganic material (neutralising agent), in at least slight excess over the amount required for neutralisation. The terms "particulate solid water-soluble alkaline inorganic material" and "neutralising agent" used herein of course include combinations of two or more such materials. If the neutralising agent is a material that itself can play a useful role in the final composition, substantially larger amounts than this may be used.

According to a preferred embodiment of the invention the neutralising agent comprises sodium carbonate, either alone or in admixture with one or more other particulate water-soluble alkaline inorganic materials, for example, sodium bicarbonate and/or sodium silicate. Sodium carbonate is of course also useful as a detergency builder and provider of alkalinity in the final composition. This embodiment of the invention may thus advantageously be used to prepare detergent powders in which sodium carbonate is the sole or principal builder, and in that case substantially more sodium carbonate than is required for neutralisation may be present.

The sodium carbonate embodiment of the invention is also suitable, however, for the preparation of detergent compositions in which substantial amounts of other builders are present. Those other builders may also advantageously be present in the high-speed mixer/granulator in step (i). Examples of such builders include crystalline and amorphous alkali metal aluminosilicates, alkali metal phosphates, and mixtures thereof. Sodium carbonate may nevertheless be present in excess of the amount required for neutralisation, in order to provide alkalinity in the product: an excess of about 10 to 15 wt% is then suitable.

The solids present in step (i) may also include any other desired solid ingredients, for example, fluorescers; polycarboxylate polymers; antiredeposition agents, for example, sodium carboxymethyl cellulose; fatty acids for in-situ neutralisation to form soaps; or fillers such as sodium sulphate, diatomaceous earth, calcite, kaolin or bentonite.

If desired, solid particulate surfactants, for example, alkylbenzene sulphonate and/or alkyl sulphate in powder form, may form part of the solids charge in step (i). Thus, for example, a detergent powder prepared by the process of the invention may contain alkylbenzene sulphonate in part introduced as a powder in step (i), and in part prepared in situ in step (ii).

Alternatively or additionally, a spray-dried detergent base powder may form part of the solids charge in step (i).

According to one preferred embodiment of the invention, the solids present in step (i) include a finely divided particulate flow aid. This is suitably present in an amount of from 2 to 8 wt%, more preferably from 5 to 7 wt%, based on the final composition. Suitable flow aids include crystalline or amorphous alkali metal aluminosilicate, thermally treated perlite, calcite, diatomaceous earth, and combinations of these.

Preferred flow aids are diatomaceous earth, and, in particular, Dicamol (Trade Mark) 424 thermally treated perlite. This material has a silica content of 80-87 wt% and a water absorbance capacity of 250-300 wt%. Its presence in the solids mix before and during the addition of the acid anionic surfactant precursor appears to assist in preventing excessive agglomeration and maintaining the reaction mix in particulate form.

It is an important feature of the process of the invention that the solids be very efficiently mixed and fluidised before the introduction of any liquid ingredients: the term "fluidisation" as used herein means a state of mechanically induced vigorous agitation in which the mass of particles is to some extent aerated, but does not necessarily imply the blowing in of a gas. This state is achieved by the choice of apparatus: a high-speed mixer/granulator having both a stirring action and a cutting action. Preferably the high-speed mixer/granulator has rotatable stirrer and cutter elements that can be operated independently of one another, and at separately changeable or variable speeds. Such a mixer is capable of combining a high-energy stirring input with a cutting action, but can also be used to provide other, gentler stirring regimes with or without the cutter in operation.

A preferred type of high-speed mixer/granulator for use in the process of the invention is bowl-shaped and preferably has a substantially vertical stirrer axis.

Especially preferred are mixers of the Fukae (Trade Mark) FS-G series manufactured by Fukae Powtech Kogyo Co., Japan; this apparatus is essentially in the form of a bowl-shaped vessel accessible via a top port, provided near its base with a stirrer having a substantially vertical axis, and a cutter positioned on a side wall. The stirrer and cutter may be operated independently of one another, and at separately variable speeds. The vessel can be fitted with a cooling jacket or, if necessary, a cryogenic unit.

A similar mixer manufactured in India is the Sapphire (Trade Mark) RMG series of rapid mixer/granulator, which like the Fukae mixer is available in a range of different sizes. This apparatus is essentially in the form of a bowl-shaped vessel raised up pneumatically to seal against a fixed lid. A three-bladed stirrer and a four-bladed cutter share a single substantially vertical axis of rotation mounted on the lid. The stirrer and cutter may be operated independently of one another, the stirrer at speeds of 75 or 100 revolutions per minute (rev/min), and the cutter at speeds of 1440 rev/min or 2880 rev/min. The vessel can be fitted with a cooling water jacket.

The Sapphire RMG-100 mixer, which is suitable for handling a 60 kg batch of detergent powder, has a bowl of about 1 metre diameter and 0.3 metres deep; the working capacity is 200 litres. The stirrer blades are of 1 metre diameter and the cutter blades are of 0.1 metre diameter.

Other similar mixers found to be suitable for use in the process of the invention include the Diosna (Trade Mark) V series ex Dierks & Söhne, Germany; and the Pharma Matrix (Trade Mark) ex T K Fielder Ltd., England. Other mixers believed to be suitable for use in the process of the invention are the Fuji (Trade Mark) VG-C series ex Fuji Sangyo Co., Japan; and the Roto (Trade Mark) ex Zanchetta & Co srl, Italy.

Yet another mixer found to be suitable for use in the process of the invention is the Lödige (Trade Mark) FM series batch mixer ex Morton Machine Co. Ltd., Scotland. This differs from the mixers mentioned above in that its stirrer has a horizontal axis. This configuration, however, has the disadvantage that mixing and fluidising in step (i) is less efficient, and may need to be supplemented by the blowing in of gas as described in the aforementioned GB 1 369 269 (Colgate).

The next stage of the process of the invention - step (ii) - is the introduction of the acid surfactant precursor. The way in which this step is conducted is crucial to the success of the process. In particular, it is important that throughout the neutralisation step the amount of liquid present never rises to a level where

it can cause substantial agglomeration.

It is believed, however, that the solids, now efficiently fluidised, have to be wetted with just sufficient water to initiate and promote the neutralisation reaction before they encounter the acid precursor. The amount of free water present in step (ii) is therefore believed to be very important. The term "free water" is used herein to mean water that is not firmly bound as water of hydration or crystallisation to inorganic materials. If insufficient is present, the reaction will not proceed rapidly, and unreacted detergent acid precursor will accumulate in the mixer and act as a binder, causing substantial agglomeration, balling up and even dough formation. Thus it would appear that enough water to wet all the solids should be present, but not so much that the water itself will act as a binder.

The solids themselves may contain sufficient free water for these conditions to be attained. For example, a spray-dried detergent base powder blown to a relatively high moisture content could provide most or all of the free water required. If insufficient free water is inherently present in the solids charge, a carefully controlled amount of water should be added either prior to or concurrently (together or separately) with the addition of the acid precursor. To ensure thorough wetting of the solids before the introduction of the acid precursor, all the water may be added before addition of the acid precursor commences. Alternatively, the acid precursor and the water may be introduced simultaneously into the mixer.

If desired, a small amount of water, sufficient to initiate the neutralisation reaction but not sufficient to cause substantial agglomeration, may be premixed with the acid precursor before the latter is introduced into the high-speed mixer/granulator. If a coloured product is desired, dyestuff may conveniently be premixed with the acid precursor and water before addition to the high-speed mixer/granulator.

The amount of water to be added will depend on the nature of the solids present. It has been found that an amount within the range of from 0.5 to 2.0 wt%, preferably from 0.5 to 1.5 wt%, based on the total solids present in steps (i) and (ii), gives good results in the preferred embodiment of the invention in which the neutralising agent is sodium carbonate.

Another important condition for step (ii) is that the acid precursor be added gradually, so that it will be consumed immediately and will not accumulate in the mixer in unreacted form. The time required and preferred for addition of the acid precursor is of course dependent on the amount to be added, but in general addition preferably takes place over a period of at least 1 minute, more preferably over a period of from 2 to 12 minutes, more preferably from 3 to 10 minutes.

Other liquid detergent ingredients may be introduced during step (ii). Examples of such ingredients include nonionic surfactants, and low-melting fatty acids which may be also be neutralised in situ, to form soaps.

The neutralisation step (ii) may typically take 2 to 12 minutes, and, as indicated above, the gradual addition of the acid precursor (optionally plus other liquid ingredients) may or may not be preceded by a separate step in which water (optionally plus other liquid ingredients) is added to the mixer.

As indicated previously, the temperature of the powder mass in the high-speed mixer/granulator should be maintained throughout step (ii) at 55 °C or below, preferably below 50 °C, more preferably below 47 °C, and desirably below 40 °C. A water jacket may be sufficient, for example, a jacket supplied with water at 25 °C is generally adequate to achieve temperatures below 47 °C; but in some cases it may be necessary to provide a cryogenic unit to inject cooling liquid or gas, for example, liquid nitrogen, into the mass of powder. If the temperature is allowed to rise, agglomeration and lump formation may occur.

A very important feature of the process of the invention is granulation in the high-speed mixer/granulator. This will generally take the form of a separate granulation step (iii) after addition of the acid precursor and neutralisation are complete. If, however, addition of the liquids takes place over a relatively long period, granulation can occur before addition is complete, and then a separate granulation step (iii) may be unnecessary. In this case, steps (ii) and (iii) of the process may be regarded as having coalesced to form a single continuous step (ii)/(iii).

The granulation or densification process leads to a product of very high bulk density. Granulation in the process of the invention requires the presence of a liquid binder, but in an amount significantly lower than that used when granulating a powder in conventional apparatus such as a pan granulator: for example, from 3 to 8 wt% of the total composition, especially about 5 wt%, as compared to 10-15 wt%. The binder is added prior to granulation but after neutralisation is complete. It will generally comprise water and/or a liquid detergent ingredient, for example, an aqueous solution of a polycarboxylate polymer, or a nonionic surfactant, or a mixture of any of these.

In calculating the amount of binder required, it is important to take into account any free water already present in the composition and releasable at the process temperature, generally about 30-50 °C. For example, hydrated zeolite (which contains 27 moles of water per mole, or about 20 wt% of bound water) might be expected to release about 20 wt% of this (4 wt% of its total weight) at these temperatures; while

sodium tripolyphosphate hexahydrate would probably release little or no water.

It is believed that the total amount of free water that can be tolerated in the whole process is limited, and generally should not amount to more than 8 wt% of the total composition, preferably not more than 4 wt%.

As with the water required for the neutralisation step (ii), sufficient free moisture for granulation may be available from the powder mass itself, and it may not be necessary to add a liquid binder.

The product of the granulation step (iii) is a particulate solid of high bulk density - at least 650 g/litre, preferably at least 750 g/litre, and more preferably at least 800 g/litre. As previously indicated, the particle size distribution is generally such that at least 50 wt%, preferably at least 70 wt% and more preferably at least 85 wt%, of particles are smaller than 1700 µm, and the level of fines is low. No further treatment has generally been found to be necessary to remove either oversize particles or fines.

If desired, further ingredients may be admixed to the granulated product of step (iii). For example, minor solid ingredients such as fluorescer and sodium carboxymethylcellulose may be added at this stage rather than included in the initial solids mix.

Although the product generally has good flow properties, low compressibility and little tendency towards caking, those powder properties may be improved further and bulk density further increased by the admixture of a builder salt or a finely divided particulate flow aid after granulation is complete.

A preferred builder salt that may be postdosed is sodium tripolyphosphate. This option is of especial interest for powders in which the principal or sole builder is sodium carbonate.

The flow aids mentioned above are also suitable for addition at this later stage in the process. Depending on the flow aid chosen, it may suitably be added in an amount of from 0.2 to 12.0 wt%, based on the total product.

Suitable flow aids include crystalline and amorphous alkali metal aluminosilicates having an average particle size within the range of from 0.1 to 20 µm, preferably from 1 to 10µm. The crystalline material (zeolite) is preferably added in an amount of from 3.0 to 12.0 wt%, more preferably from 4.0 to 10.0 wt%, based on the total product. The amorphous material, which is more weight-effective, is preferably added in an amount of from 0.2 to 5.0 wt%, more preferably from 0.5 to 3.0 wt%, based on the total product. A suitable amorphous material is available commercially from Crosfield Chemicals Ltd, Warrington, Cheshire, England, under the trade mark Alusil. If desired, both crystalline and amorphous aluminosilicates may be used, together or sequentially, as flow aids.

The other flow aids mentioned previously, namely, thermally treated perlite, calcite, and diatomaceous earth, are also suitably used in amounts of from 0.2 to 5.0 wt%, preferably from 0.5 to 3.0 wt%, based on the total product.

Yet other flow aids suitable for use in the process of the invention include precipitated silica, for example, Neosyl (Trade Mark), and precipitated calcium silicate, for example, Microcal (Trade Mark), both commercially available from Crosfield Chemicals Ltd.

A process which comprises admixing finely divided amorphous sodium aluminosilicate to a dense granular detergent composition containing surfactant and builder and prepared and/or densified in a high speed mixer/granulator is described and claimed in our copending EP-A-339996 filed on 27 April 1989.

The product

As already indicated, the process of the invention produces a granular high-bulk-density solid, containing surfactant and builder, and having a bulk density of at least 650 g/litre and preferably at least 700 g/litre. It is also characterised by an especially low particle porosity, preferably not exceeding 0.25 and more preferably not exceeding 0.20, which distinguishes it from even the densest powders prepared by spray-drying.

This final granulate may be used as a complete detergent composition in its own right. Alternatively, it may be admixed with other components or mixtures prepared separately, and may form a major or minor part of a final product. Generally, any additional ingredients such as enzymes, bleach and perfume that are not suitable for undergoing the granulation process and the steps that precede it may be admixed to the granulate to make a final product. The densified granulate may typically constitute from 40 to 100 wt% of a final product.

In another embodiment of the invention, the densified granulate prepared in accordance with the present invention is an "adjunct" comprising a relatively high level of detergent-active material on an inorganic carrier; and this may be admixed in a minor amount with other ingredients to form a final product.

The process may with advantage be used to prepare detergent compositions containing from 5 to 45 wt%, especially from 5 to 35 wt%, of anionic surfactant, this anionic surfactant being derived wholly or in

part from the in-situ neutralisation reaction of step (ii).

The process of the invention is of especial interest for the production of detergent powders or components containing relatively high levels of anionic surfactant, for example, 15 to 30 wt%, more especially 20 to 30 wt%, but it is equally useful for the preparation of powders containing lower levels of anionic surfactant.

The anionic surfactant prepared at least in part by in-situ neutralisation may, for example, be selected from linear alkylbenzene sulphonates, alpha-olefin sulphonates, internal olefin sulphonates, fatty acid ester sulphonates and combinations thereof. The process of the invention is especially useful for producing compositions containing alkylbenzene sulphonates, by in-situ neutralisation of the corresponding alkylbenzene sulphonic acid.

Other anionic surfactants that may be present in compositions prepared by the process of the invention include primary and secondary alkyl sulphates, alkyl ether sulphates, and dialkyl sulphosuccinates. Anionic surfactants are of course well known and the skilled reader will he able to add to this list by reference to the standard textbooks on this subject.

If an especially high content of anionic surfactant in the final product is desired, additional anionic surfactant, in salt form (generally aqueous paste or solution) rather than in acid precursor form, may be added after granulation. In one preferred embodiment of the invention, the post-added anionic surfactant is alpha-olefin sulphonate. The possible addition of solid particulate anionic surfactant at an earlier stage in the process has already been mentioned. Thus the process of the invention represents a versatile route for incorporating high levels of anionic surfactant in powders of high bulk density.

As previously indicated, nonionic surfactants may also be present. These too are well known to those skilled in the art, and include primary and secondary alcohol ethoxylates.

Other types of non-soap surfactant, for example, cationic, zwitterionic, amphoteric or semipolar surfactants, may also be present if desired. Many suitable detergent-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

If desired, soap may also be present, to provide foam control and additional detergency and builder power.

Typically, detergent compositions produced by the process of the invention may comprise from 10 to 35 wt% of anionic surfactant, from 0 to 10 wt% of nonionic surfactant, and from 0 to 5 wt% of fatty acid soap.

Typical products of the invention

The following are general, non-limiting examples of formulation types that may readily be prepared by the process of the invention.

(1) Compositions comprising:

(a) from 5 to 45 wt% of anionic surfactant,

(b) from 20 to 70 wt% of inorganic builder salt comprising crystalline or amorphous alkali metal aluminosilicate, sodium tripolyphosphate, sodium carbonate, sodium silicate or any combination thereof,

(c) from 0 to 20 wt% of filler and/or flow aid comprising diatomaceous earth, silica, calcite, sodium sulphate, bentonite, kaolin or any combination thereof,

and optionally other detergent ingredients to 100 wt%.

In particular:

(1a) compositions containing sodium tripolyphosphate as the principal builder, and also containing sodium carbonate as neutralising alkali:

(a) from 15 to 30 wt% of of anionic surfactant,

(b1) from 10 to 60 wt% of sodium tripolyphosphate,

(b2) from 5 to 60 wt% of sodium carbonate,

(c) from 0 to 20 wt% of filler and/or flow aid comprising diatomaceous earth, silica, calcite, sodium sulphate, bentonite, kaolin or any combination thereof,

and optionally other detergent ingredients to 100 wt%; and

(1b) compositions containing sodium carbonate as the principal builder:

(a) from 15 to 30 wt% of of anionic surfactant,

(b) from 20 to 70 wt% of sodium carbonate,

(c) from 0 to 20 wt% of filler and/or flow aid comprising diatomaceous earth, silica, calcite, sodium sulphate, bentonite, kaolin or any combination thereof,

and optionally other detergent ingredients to 100 wt%.

(2) Compositions containing crystalline or amorphous alkali metal aluminosilicate, especially crystalline zeolite and more especially zeolite 4A, as a detergency builder:

(a) from 5 to 35 wt% of non-soap detergent-active material consisting at least partially of anionic surfactant,

(b) from 15 to 45 wt% (anhydrous basis) of crystalline or amorphous alkali metal aluminosilicate,

and optionally other detergent ingredients, including any excess of the neutralising agent for the anionic surfactant, to 100 wt%. The weight ratio of (b) to (a) is preferably at least 0.9:1.

An especially preferred class of detergent compositions that may be prepared by the process of the invention is described and claimed in our copending EP-A-340013 filed on 27 April 1989. These compositions comprise:

(a) from 17 to 35 wt% of non-soap detergent-active material consisting at least partially of anionic surfactant, and

(b) from 28 to 45 wt% of crystalline or amorphous alkali metal aluminosilicate,

the weight ratio of (b) to (a) being from 0.9:1 to 2.6:1, preferably from 1.2:1 to 1.8:1, and optionally other detergent ingredients to 100 wt%.

(3) Compositions as described in our copending EP-A-351937 filed on 27 April 1989:

(a) from 12 to 70 wt% of non-soap detergent-active material, and

(b) at least 15 wt% of water-soluble crystalline inorganic salts, including sodium tripolyphosphate and/or sodium carbonate,

the weight ratio of (b) to (a) being at least 0.4:1, preferably from 0.4:1 to 9:1 and more preferably from 0.4:1 to 5:1, and optionally other detergent components to 100 wt%.

These compositions preferably contain a total of from 15 to 70 wt% of water-soluble crystalline inorganic salts, which may comprise, for example, sodium sulphate, sodium ortho- or pyrophosphate, or sodium meta- or orthosilicate. Especially preferred compositions contain from 15 to 50 wt%, more preferably from 20 to 40 wt%, of sodium tripolyphosphate.

As previously indicated, all these preferred classes of detergent composition that may be prepared by the process of the invention may contain conventional amounts of other conventional ingredients, for example, bleaches, enzymes, lather boosters or lather controllers as appropriate, antiredeposition and antiincrustation agents, perfumes, dyes and fluorescers. These may be incorporated in the product at any suitable stage, and the skilled detergent formulator will have no difficulty in deciding which ingredients are suitable for admixture in the high-speed mixer/granulator, and which are not. The process of the invention has the advantage over conventional spray-drying processes that no elevated temperatures are involved, so fewer restrictions are imposed on the way in which heat-sensitive ingredients such as bleaches and enzymes are incorporated into the product.

The invention is further illustrated by the following non-limiting Examples, in which parts and percentages are by weight unless otherwise stated.

EXAMPLES

Example 1

A 750 kg batch of high-bulk-density detergent powder having the following nominal formulation was prepared using a Fukae (Trade Mark) FS-1200 high-speed mixer/granulator:

	wt%
Linear alkylbenzene sulphonate	25.0
Nonionic surfactant	2.0
Soap	1.0
Zeolite 4A (anhydr.))	(35.0
Water with zeolite)	(9.99
Sodium silicate	4.0
Acrylate/maleate copolymer	1.0
Sodium sulphate	1.77
Fluorescer	0.18
Sodium carboxymethyl cellulose	0.9
Sodium carbonate	15.5
Total added water	2.0
Speckles	0.8
Enzyme	0.6
Perfume	0.25

	100.00

The ratio of zeolite (anhydrous) to total non-soap surfactant in this composition was 1.29:1.

The process was carried out as follows:

(i) Solid ingredients as specified below were dry-mixed in the Fukae mixer for 1 minute, using a stirrer speed of 100 rev/min and a cutter speed of 200 rev/min.

	parts
Zeolite 4A (hydrated)	34.0
Sodium carbonate	19.53*
Sodium carboxymethylcellulose	0.9
Sodium silicate	4.0
Acrylic/maleic copolymer	1.0
Fluorescer	0.9
Fatty acid	0.92
Total solids	61.25

*This amount of sodium carbonate represented a 4.9x excess over that required for neutralisation of the alkylbenzene sulphonic acid (see paragraph (ii) below).

(ii) Water (0.375 parts, = 0.61 wt% on total solids) was added, and the mixer was operated at the same stirrer and cutter speeds for 1 minute 30 seconds. Linear alkylbenzene sulphonic acid (23.5 parts) was added over a period of 5 minutes while the mixer was operated at a stirrer speed of 80 rev/min and a cutter speed of 2000 rev/min. The temperature was maintained below 50 °C by means of a cooling jacket filled with water. Throughout this step, the reaction mixture remained in particulate form.

Total liquids	23.88
Solids as % of total	71.95

The liquid : solid ratio at the end of step (ii) was 0.39.

(iii) When neutralisation was complete, binder in the form of further water (1.4 parts), and nonionic surfactant (2.0 parts), were added to the mixer, which was then operated for 3 minutes at a stirrer speed of 100 rev/min and a cutter speed of 2000 rev/min to effect granulation. The temperature was maintained below 50 °C by means of a cooling jacket filled with water. The product of this step was a granular solid.

Total liquids	27.28
Solids as % of total	69.19

The liquid : solid ratio at the end of step (iii) was 0.44.

(iv) Zeolite (a further 11 parts) was then added as a flow aid, while the mixer was operated for 2 minutes at a stirrer speed of 90 rev/min with the cutter turned off.

The resulting powder was free-flowing, had a bulk density of 850 g/litre, and contained 73 wt% of particles <1700 µm. The particle porosity was 0.15.

Coloured speckles of the same powder (0.8 parts) and enzyme granules (0.6 parts) were mixed with the powder using a rolling drum, and perfume (0.25 parts) were sprayed on, to give a fully formulated high-bulk-density detergent powder having excellent powder properties.

Example 2

The procedure of Example 1 was repeated, with the difference that the nonionic surfactant was added as a mixture with the acid, instead of during step (iii). A similar powder was obtained.

Example 3

The procedure of Example 1 was repeated, with the difference that 5 parts of zeolite were added to the mixer during step (iii), after addition of the binder but before granulation, and only 6 parts of zeolite were added as a flow aid in step (iv). A similar powder was obtained.

Example 4

The procedure of Example 2 was repeated, with the difference that half the anionic surfactant was added in step (i) as a powder (Marlon (Trade Mark) A390 ex Hüls). A similar powder was obtained.

Example 5

This Example illustrates a procedure in which in-situ neutralisation is followed by the addition of a spray-dried base powder, and the mix is granulated together in the high-speed mixer/granulator.

A 750 kg batch of high-bulk-density detergent powder having the following nominal formulation was prepared using a Fukae (Trade Mark) FS-1200 high-speed mixer/granulator:

			parts
Linear alkylbenzene sulphonate			25.0
Nonionic surfactant			2.0
Soap			1.0
Zeolite 4A (anhydr.)	)	(	35.0
Water with zeolite	)	(	10.0
Sodium silicate			4.0
Acrylate/maleate copolymer			1.0
Sodium sulphate			1.8
Fluorescer			0.18
Sodium carboxymethyl cellulose			0.9
Sodium carbonate			15.5
			96.4

The ratio of zeolite (anhydrous) to total non-soap surfactant in this composition was 1.29:1.

The process was carried out as follows:

(i) Solid ingredients as specified below were dry-mixed in the Fukae mixer for 1 minute, using a stirrer speed of 100 rev/min and a cutter speed of 2000 rev/min.

	kg
Zeolite 4A (hydrated)	126
Sodium carbonate	93.1*
Sodium carboxymethylcellulose	3.4
Sodium silicate	15.2
Acrylic/maleic copolymer	3.8
Fatty acid	3.5
Fluorescer	0.7
Total solids	245.7

*5.98x excess over amount required for neutralisation

(ii) Water (3 kg, = 1.22 wt% on total solids) was added, and the mixer was operated at a stirrer speed of 60 rev/min and a cutter speed of 2000 rev/min for 1 minute. The following liquid mix was then added over a period of 3 minutes while the mixer was operated at the same stirrer and cutter speeds:

Linear alkylbenzene sulphonic acid	89.1
Nonionic surfactant	11.4
Total liquids (including water)	103.5

The solids therefore represented 70.4 wt% of the liquids/solids mix during the neutralisation step.

The liquid : solid ratio at the end of the neutralisation step was 0.42. The temperature was maintained below 50 °C by means of a cooling jacket filled with water.

Throughout this step, the reaction mixture remained in particulate form.

(iii) When neutralisation was complete, a spray-dried base powder (336 kg) of the following formulation was added to the mixer:

			parts
Linear alkylbenzene sulphonate			25.0
Nonionic surfactant			1.0
Soap			1.0
Zeolite 4A (anhydr.)	)	(	35.0
Water with zeolite	)	(	10.0
Sodium silicate			4.0
Acrylate/maleate copolymer			1.0
Sodium sulphate			1.8
Fluorescer			0.18
Sodium carboxymethyl cellulose			0.9
Sodium carbonate			10.5
Water			3.0

and the whole mix granulated for 4 minutes at a stirrer speed of 80 rev/min and a cutter speed of 2000 rev/min. The spray-dried powder contained sufficient free water, in addition to that added during step (ii), that no further addition of water as binder was necessary.

(iv) Zeolite (a further 60 kg) was then added as a flow aid, while the mixer was operated for 1 minute at a stirrer speed of 80 rev/min with the cutter turned off.

The resulting powder was free-flowing, had a bulk density of 891 g/litre, and contained 80 wt% of particles <1700 µm.

Examples 6 and 7

This pair of Examples illustrates the benefit of cooling with liquid nitrogen during the neutralisation step (ii).

Two 750 kg batches (Examples 6 and 7) of high-bulk-density detergent powder having the nominal formulation given in Example 5 was prepared using the Fukae FS-1200 high speed mixer/granulator. The process was carried out as follows:

(i) Solid ingredients as specified below were dry-mixed in the Fukae mixer for 1 minute, using a stirrer speed of 100 rev/min and a cutter speed of 2000 rev/min.

	kg
Zeolite 4A (hydrated)	285
Sodium carbonate	148
Sodium carboxymethylcellulose	6.8
Sodium silicate	30.4
Acrylic/maleic copolymer	7.6
Fatty acid	7.0
Total solids	484.8

(ii) Water (6 kg, = 1.24 wt% on total solids) was added, and the mixer was operated at a stirrer speed of 75 rev/min and a cutter speed of 2000 rev/min for 1 minute. The following liquid mix was then added over 5 minutes while the mixer was operated at the same stirrer and cutter speeds:

Linear alkylbenzene sulphonic acid	178
Nonionic surfactant	15
Total liquids (including water)	199
Solids as % of total	70.9
Liquid : solid ratio	0.41

After addition of the liquids was complete the mixer speeds were increased to 100 rev/min/2000 rev/min for 2 minutes. For Example 6, the temperature was maintained below 35 °C throughout the neutralisation step by spraying liquid nitrogen into the powder. For Example 7, the liquid nitrogen cooling was omitted, and the temperature rose to 52 °C. In both Examples, the reaction mixture remained in particulate form throughout the neutralisation step.

(iii) When neutralisation was complete, binder in the form of further water (6 kg) was added to the mixer at stirrer/cutter speeds of 80 rev/min/2000 rev/min, and the mixer was then operated for 3 minutes at the same stirrer and cutter speeds to effect granulation.

(iv) Zeolite (a further 57 kg) as a flow aid, and fluorescer (1.4 kg) were then added, while the mixer was operated for 1 minute at a stirrer speed of 80 rev/min with the cutter turned off.

The powder of Example 6 was free-flowing, had a bulk density of 821 g/litre, and contained 81 wt% of particles <1700 µm.

The powder of Example 7 was a product of similar bulk density but containing only 69 wt% of particles <1700 µm.

Example 8

A 20 kg batch of high-bulk-density detergent powder having the following nominal formulation was prepared using a Fukae FS-30 high-speed mixer/granulator:

	wt%
Linear alkylbenzene sulphonate	23.34
Nonionic surfactant	1.5
Soap	0.7
Zeolite 4A (anhydr.)	(35.83
Water with zeolite	(10.17
Sodium silicate	4.0
Acrylate/maleate copolymer	2.0
Sodium sulphate	1.72
Fluorescer	0.18
Sodium carboxymethyl cellulose	0.9
Sodium carbonate	15.0
Added water	2.0
Speckles	0.8
Enzyme	0.61
Perfume	0.25
Flow aid	1.0
	100.00

The ratio of zeolite (anhydrous) to total non-soap surfactant in this composition was 1.44:1.

The process was carried out as follows:

(i) Solid ingredients as specified below were dry-mixed in the Fukae mixer for 1 minute, using a stirrer speed of 300 rev/min and a cutter speed of 3000 rev/min.

	parts
Zeolite 4A (hydrated)	38.5
Sodium carbonate	18.72*
Sodium carboxymethylcellulose	0.9
Sodium silicate	4.0
Total solids	62.12

*This amount of sodium carbonate represented an approximately 5x excess over the amount required for neutralisation of the alkylbenzene sulphonic acid and fatty acid (see paragraph (ii) below): the excess corresponds to the 15.0 wt% present in the final formulation to provide alkalinity.

(ii) Water (0.375 parts, = 0.61 wt% on total solids) was added, and the mixer was operated at a stirrer speed of 100 rev/min and a cutter speed of 3000 rev/min for 1 minute 30 seconds. The following liquid mixture was added over a period of 5 minutes while the mixer was in operation at the came stirrer and cutter speeds:

	parts
Linear alkylbenzene sulphonic acid	21.85
Fatty acid	0.65
Nonionic surfactant	1.5
Total liquids	24.00
Solids as % of total	72.13
Liquid : solid ratio	0.39

The temperature was maintained below 50 °C by means of a cooling jacket filled with water. Throughout this step, the reaction mixture remained in particulate form.

(iii) When neutralisation was complete, the following binder mixture was added:

	parts
Water	1.0
Acrylic/maleic copolymer	2.0
Fluorescer	0.9
Total liquids	27.9
Solids as % of total	69.0
Liquid : solid ratio	0.45

The mixer was then operated for 3 minutes at a stirrer speed of 300 rev/min and a cutter speed of 3000 rev/min to effect granulation. The temperature was maintained below 50 °C by means of a cooling jacket filled with water. The product of this step was a granular solid.

(iv) 7.5 parts of zeolite, and 1 part of amorphous sodium aluminosilicate (Alusil (Trade Mark) ex Crosfield Chemicals Ltd, 1 part) were then added as a flow aid, while the mixer was operated for 2 minutes at a stirrer speed of 90 rev/min with the cutter turned off.

The resulting powder was free-flowing, had a bulk density of 830 g/litre, and contained 85 wt% of particles <1700 μm.

Coloured speckles of the same powder (0.8 parts) and enzyme granules (0.61 parts) were mixed with the powder using a rolling drum, and perfume (0.25 parts) were sprayed on, to dive a fully formulated high-bulk-density detergent powder having excellent powder properties.

Example 9

A 20 kg batch of high-bulk-density detergent powder built with sodium tripolyphosphate and sodium carbonate and having the following nominal formulation was prepared using a Fukae FS-30 high-speed

mixer/granulator:

	parts
Linear alkylbenzene sulphonate	32.0
Sodium tripolyphosphate	22.0
Sodium carbonate	40.0
Added water	2.0
Minor ingredients	0.7
Alusil flow aid	2.0
	98.70

The ratio of crystalline water-soluble inorganic salts to total non-soap surfactant in this composition was 1.9:1.

In this formulation sodium carbonate was present as a major part of the building system. The sodium carbonate introduced during step (i) (see below) amounted to an approximately 8x excess over the amount required for neutralisation of the alkylbenzene sulphonic acid (see paragraph (ii) below).

The process was carried out as follows:

(i) The solid ingredients were dry-mixed in the Fukae mixer for 1 minute, using a stirrer speed of 300 rev/min and a cutter speed of 3000 rev/min:

	parts
Sodium carbonate	44.92
Sodium tripolyphosphate	22.0
Dry minor ingredients	0.7
Total solids	67.62

(ii) Water (2 parts) was added, and the mixer was operated at a stirrer speed of 100 rev/min and a cutter speed of 3000 rev/min for 1 minute. The linear alkylbenzene sulphonic acid (29.96 parts) was added over a period of 1 minute while the mixer was in operation at the same stirrer and cutter speeds. The temperature was maintained below 50 °C by means of a cooling jacket filled with water. Throughout this step, the reaction mixture remained in particulate form.

Total liquids	31.96
Solids as % of total	67.90
Liquid : solid ratio	0.47

(iii) When neutralisation was complete, binder in the form of further water (4.0 parts) was added to the mixer, while it was operated for 1 minute at a stirrer speed of 100 rev/min and a cutter speed of 3000 rev/min. The mixer was which was then operated for 4 minutes at a stirrer speed of 300 rev/min and a cutter speed of 3000 rev/min to effect granulation. The temperature was maintained below 50 °C by means of a cooling jacket filled with water. The product of this step was a granular solid.

Total liquids	35.96
Solids as % of total	65.28
Liquid : solid ratio	0.53

(iv) Alusil (2 parts) was then added as a flow aid, while the mixer was operated for 1 minute at a stirrer speed of 90 rev/min with the cutter turned off.

The resulting detergent powder was free-flowing, had a bulk density of 875 g/litre, and contained 75 wt% of particles <1700 μm. Powder properties were excellent: dynamic flow rate was 133 ml/s and compressibility was 2% v/v.

Example 10

A 750kg batch of high-bulk-density detergent powder built with sodium tripolyphosphate and sodium carbonate and having the following nominal formulation was prepared using a Fukae FS-1200 high-speed mixer/granulator:

	wt%
Linear alkylbenzene sulphonate	25.0
Soap	2.0
Sodium tripolyphosphate	38.0
Sodium silicate	5.0
Sodium carbonate	18.2
Sodium sulphate	6.6
Fluorescer	0.2
Alusil flow aid	3.0
Added water	2.0
	100.0

The ratio of crystalline water-soluble inorganic salts to total non-soap surfactant in this composition was 2.5:1.

The process was carried out as follows:

(i) The solid ingredients were dry-mixed in the Fukae mixer for 1 minute, using a stirrer speed of 100 rev/min and a cutter speed of 1200 rev/min.

Sodium carbonate	22.04
Sodium tripolyphosphate	38.0
Sodium sulphate	6.6
Dry minor ingredients	0.2
Total solids	66.84

(ii)/(iii) Water and alkylbenzenesulphonic acid were added over a period of 10 minutes while the mixer was operated at a stirrer speed of 35 rev/min and a cutter speed of 1200 rev/min. The temperature was maintained at about 45°C by means of a cooling jacket filled with water. Because of the rather slow addition of the acid, it was found that granulation had occurred as soon as acid addition was complete. Thus no separate granulation step was required.

Water	0.8
Alkylbenzene sulphonic acid	23.4
Total liquids	24.2
Solids as % of total	73.41
Liquid : solid ratio	0.36

(iv) Alusil was added as a flow aid, while the mixer was operated for 1.5 minutes at a stirrer speed of 80 rev/min and a cutter speed of 1200 rev/min.

The resulting detergent powder was free-flowing, had the extremely high bulk density of 1050 g/litre, and contained about 70 wt% of particles <1700 μm. Dynamic flow rate was 71 ml/s and compressibility was 4.7% v/v.

Example 11

A 60 kg batch of high-bulk-density detergent powder having the following nominal formulation was prepared using a Sapphire (Trade Mark) RMG-100 high-speed mixer/granulator:

	wt%
Linear alkylbenzene sulphonate	29.0
Sodium tripolyphosphate	35.0
Sodium carbonate	20.0
Flow aid (Dicamol 424)[1]	5.0
Sodium carboxymethylcellulose	1.5
Fluorescer (Photine C)	0.3
Blue dye (phthalocyanine)	0.1
Perfume	0.1
Flow aid (Dicamol 424)[2]	1.0
Water[3]	5.0
Salts etc to	100.0

[1] Added before neutralisation (see below)
[2] Added after neutralisation (see below)
[3] Added water about 1-1.5 wt%; the rest is from the raw materials and generated by the neutralisation reaction.

The process was carried out as follows:

(i) Solid ingredients as specified below were dry-mixed in the Sapphire mixer for 1 minute, using a stirrer speed of 75 rev/min and a cutter speed of 2880 rev/min.

	parts
Sodium tripolyphosphate	35.0
Sodium carbonate	25.76*
Flow aid (Dicamol 424)	5.0

*This amount of sodium carbonate represented a 4.47x excess over that required for neutralization of the alkylbenzene sulphonic acid (see paragraph (ii) below).

(ii) A liquids premix was prepared by mixing 0.1 parts of phthalocyanine blue dye and 1.0 part water with a Silverson mixer, then mixing the resulting dye dispersion into 29.19 parts of alkylbenzene sulphonic acid of 93 wt% purity, also with the Silverson mixer.

The liquids premix was then added to the solids mix in the Sapphire mixer at a liquid to solid ratio of 0.47 over a period of 5 minutes while the mixer was operated at a stirrer speed of 75 rev/min and a cutter speed of 2880 rev/min. The temperature was maintained below 50 °C by means of a cooling jacket filled and circulated with water at 25 °C. Throughout this step, the reaction mixture remained in particulate form.

(iii) When neutralisation was complete, the cutter speed was reduced to 1440 rev/min while the stirrer speed remained at 75 rev/min, and minor solids (sodium carboxymethyl cellulose, fluorescer) were added over a 1-minute period, together with further flow aid (Dicamol 424). The resulting mix was granulated for a further 1 minute at a stirrer speed of 75 rev/min and a cutter speed of 2880 rev/min. The material was then discharged over a 1-minute period with the cutter turned off and the stirrer running at 75 rev/min.

The resulting powder was free-flowing, homogeneously blue coloured, had a bulk density of 800 g/litre, and contained 90 wt% of particles <1700 µm. The mean particle size was 539 µm. Dynamic flow rate was 81.1 ml/s, and compressibility was 9.2% v/v.

The powder had a rapid rate of dissolution comparable with the best high-bulk-density powders presently on the market:

Time (seconds)	Dissolution (wt%)
0	64.9
15	78.5
20	86.1
25	89.5

A sample was examined by scanning electron micrography and was found to have a much more porous surface than a similar powder made without the addition of the flow aid Dicamol 424 to the initial solids mix.

Examples 12 to 14

These Examples illustrate the benefits of adding a flow aid (in this case calcite, Forcal (Trade Mark) U) during the initial stage - step (i) - of the process.

Three 60 kg batches of high-bulk-density detergent powder having the following nominal formulation was prepared using a Sapphire (Trade Mark) RMG-100 high-speed mixer/granulator:

	wt%
Linear alkylbenzene sulphonate	29.0
Sodium tripolyphosphate	35.0
Sodium carbonate	20.0
Flow aid	see below
Sodium carboxymethylcellulose	1.5
Fluorescer (Photine C)	0.3
Blue dye (phthalocyanine)	0.1
Perfume	0.1
Water	5.0
Salts etc to	100.0

The powders were prepared generally as described in Example 1, with the following differences relating to the addition of flow aid:

	Before neutralisation	After neutralisation
Example 12:	5 parts Forcal U	2 parts Dicamol 424
Example 13:	-	5 parts Forcal U after part neutralisation; 1.5 parts Dicamol 424 after neutralisation complete.
Example 14:	-	5 parts Forcal U) 1 part Dicamol 424)

The liquid to solid ratios at the end of the neutralisatior step in these Examples were therefore 0.55, 0.57 and 0.60 respectively.

All three powders were free-flowing, homogeneously blue coloured, and had bulk densities greater than 700 g/litre. Other powder properties were as follows:

	12	13	14
Yield <1700 µm (wt%)	90.3	81.2	83.1
Average particle size (µm)	607	709	699
Dynamic flow rate (ml/s)	120	120	125
Bulk density (g/l)	765	780	800
Dissolution (wt%):			
after 10 sec	56.5	33.8	27.7
after 30 sec	71.4	49.7	47.8

These results show that the sequence of addition used in Example 12 gave a powder with a smaller average particle size and a superior rate of dissolution.

Examples 15 to 19

These Examples show the effects of different flow aids added before neutralisation.

60 kg batches of powder were prepared by the general procedure used in previous Examples, but using different amounts of different flow aid as follows:

Example	Liquid: solid	Flow aid in step (i)	Flow aid in step (ii)
15	0.55	zeolite (5 parts)	Dicamol (1 part)
16	0.49	Dicamol (5 parts)	-
17	0.53	Forcal U (5 parts)	Dicamol (2 parts)
18	0.51	Filtroseem (5 pts)	Dicamol (1.5 pts)
19	0.56	Dicamol (5 parts)	Dicamol (1 part)

Powder properties are shown in the following table. It will be seen that Example 19 gave the best combination of properties.

	15	16	17
Bulk density (g/litre)	730	736	720
Yield <1700 µm (wt%)	82.5	90.0	85.0
Average particle size (µm)	723	539	640
Dynamic flow rate (ml/s)	110	81	100
Compressibility (%v/v)	10.5	10.0	15.8
Dissolution (wt%):			
after 15 sec	38.3	64.9	43.9
after 30 sec	58.2	78.5	63.7

	18	19
Bulk density (g/litre)	751	736
Yield <1700 µm (wt%)	85.6	86.3
Average particle size (µm)	536	560
Dynamic flow rate (ml/s)	115	115
Compressibility (%v/v)	11.8	11.0
Dissolution (wt%):		
after 15 sec	55.4	58.8
after 30 sec	74.6	78.2

Examples 20 to 22

The general procedure of earlier Examples was repeated, but to give powders containing a mixed surfactant system of alkylbenzene sulphonate (prepared by neutralisation) and alpha-olefin sulphonate (post-added as 4 wt% aqueous solution). The formulations were as follows:

	20	21	22
Alkylbenzene sulphonate	26.1	26.1	22.7
Olefin sulphonate	2.9	2.9	5.0
Sodium tripolyphosphate	35.0	35.0	32.0
Sodium carbonate	20.0	20.0	20.0
Flow aid (Dicamol)[1]	5.0	5.0	-
Flow aid (calcite)[1]	-	-	2.0
Sodium carboxymethylcellulose	1.5	1.5	1.5
Fluorescer	0.3	0.3	0.3
Perfume	0.1	0.1	0.1
Flow aid (Dicamol)[2]	1.0	0.5	2.0
Salts, water etc to	100.0	100.0	100.0

[1] Added before neutralisation
[2] Added after neutralisation

The powder properties of Examples 20 and 21, as shown in the following table, were not significantly different from those of Example 19. The powder of Example 22 had a higher bulk density but inferior flow properties.

	20	21	22
Bulk density (g/litre)	780	780	830
Yield <1700 µm (wt%)	87.1	84.3	89.8
Average particle size (µm)	527	578	443
Dynamic flow rate (ml/s)	100	103	67
Compressibility (%v/v)	12.6	13.8	-
Dissolution (wt%):			
after 15 sec	58.9	48.5	-
after 30 sec	75.7	68.3	77.7

Examples 23 to 25

The general procedure of earlier Examples was used to prepare sodium tripolyphosphate-built detergent powders having the following formulations:

	23	24	25
Alkylbenzene sulphonate	29.8	25.1	24.3
Sodium tripolyphosphate	52.0	20.0	35.0
Sodium carbonate	8.0	45.0	25.0
Flow aid (calcite)[1]	-	2.0	5.0
Sodium carboxymethylcellulose	1.5	1.5	1.5
Fluorescer (Photine C)	0.3	0.3	0.3
Perfume	0.1	0.1	0.1
Flow aid (Dicamol 424)[2]	-	2.0	2.0
Water, salts etc to	100.0	100.0	100.0
Liquid:solid ratio	0.60	0.42	0.45

[1] Added before neutralisation
[2] Added after neutralisation

Powder properties were as follows:

	23	24	25
Bulk density (g/litre)	800	800	830
Yield <1700 µm (wt%)	84.0	93.3	89.4
Dynamic flow rate (ml/s)	85	80	120
Average particle size (µm)	742	455	-

Examples 26 to 29

The general procedure of earlier Examples was used to produce 60 kg batches of sodium carbonate-built powders to the formulations shown below. In Examples 27 and 28, the alpha-olefin sulphonate was post-added in the form of 70 wt% paste; in Example 29 it was added as 40 wt% solution, after neutralisation but before the addition of the greater part of the calcite.

	26	27
Linear alkylbenzene sulphonate	19.0	18.9
Alpha-olefin sulphonate	-	5.0
Sodium carbonate	67.0	61.0
Flow aid (calcite)	4.0	4.0
Sodium carboxymethylcellulose	1.5	1.5
Fluorescer (Photine C)	0.2	0.2
Perfume	0.1	0.1
Flow aid (Dicamol 424)	2.0	2.0
Water, salts etc to	100.0	100.0
Liquid:solid ratio	0.36	0.50

	28	29
Linear alkylbenzene sulphonate	20.7	22.5
Alpha-olefin sulphonate	5.0	2.5
Sodium carbonate	62.0	58.0
Flow aid (calcite)	4.0	5.0
Sodium carboxymethylcellulose	1.5	1.5
Fluorescer (Photine C)	0.2	0.2
Perfume	0.1	0.1
Flow aid (Dicamol 424)	2.0	2.0
Water, salts etc to	100.0	100.0
Liquid:solid ratio	0.50	0.44

Powder properties were as follows:

-	26	27
Bulk density (g/litre)	800	800
Yield <1700 µm (wt%)	93.7	95.7
Dynamic flow rate (ml/s)	37.5*	70.0
Average particle size (µm)	-	507

*It was found that the poor flow properties of the powder of Example 16 could be substantially improved by postdosing a small amount of sodium tripolyphosphate: 7.5 wt% sodium tripolyphosphate improved the dynamic flow rate to 55.5 ml/s; 15.0 wt% sodium tripolyphosphate improved the dynamic flow rate to 60.0 ml/s.

	28	29
Bulk density (g/litre)	880	796
Yield <1700 µm (wt%)	92.8	90.0
Dynamic flow rate (ml/s)	75	92
Compressibility (% v/v)	-	13.2
Average particle size (µm)	491	268

Claims

1. A process for the preparation of a granular detergent composition or component having a bulk density of at least 650 g/litre, which process includes the step of neutralising a liquid acid precursor of an anionic surfactant with a solid water-soluble alkaline inorganic material, the process being characterised by the steps of:
   (i) fluidising a particulate solid water-soluble alkaline inorganic material in an amount in excess of that required for neutralisation, optionally in admixture with one or more other particulate solids, in a high-speed mixer/granulator having both a stirring action and a cutting action;
   (ii) gradually adding the acid precursor to the high-speed mixer/granulator while maintaining a temperature not higher than 55°C, whereby neutralisation of the acid precursor by the water-soluble alkaline inorganic material occurs while the mixture remains in particulate form;
   (iii) granulating the mixture in the high-speed mixer/granulator, in the presence of a liquid binder,
   whereby a granular detergent composition or component having a bulk density of at least 650 g/litre is formed.

2. A process as claimed in claim 1, characterised in that the particulate water-soluble alkaline inorganic material comprises sodium carbonate.

3. A process as claimed in claim 2, characterised in that the particulate water-soluble alkaline inorganic material comprises sodium carbonate in admixture with sodium bicarbonate and/or sodium silicate.

4. A process as claimed in any preceding claim, characterised in that the acid precursor is a linear alkylbenzene sulphonic acid.

5. A process as claimed in any preceding claim, characterised in that the liquids to solids ratio at the end of step (ii) is not greater than 0.60.

6. A process as claimed in any preceding claim, characterised in that in step (ii) the acid precursor is added over a period of from 2 to 12 minutes.

7. A process as claimed in any preceding claim, characterised in that water is introduced prior to or together with the acid precursor in step (ii), in an amount of from 0.5 to 2.0 wt% based on the total solids present in steps (i) and (ii).

8. A process as claimed in any preceding claim, characterised in that the solids present in step (i) comprise sodium carbonate in admixture with one or more detergency builders selected from crystalline and amorphous alkali metal aluminosilicates, alkali metal phosphates, and mixtures thereof.

9. A process as claimed in any preceding claim, characterised in that the solids present in step (i) further include a surfactant in powder form.

10. A process as claimed in any preceding claim, characterised in that the solids present in step (i) include a spray-dried detergent base powder.

11. A process as claimed in any preceding claim, characterised in that the particulate solids present during step (i) include a finely divided particulate flow aid.

12. A process as claimed in claim 11, characterised in that the flow aid is zeolite, amorphous alkali metal aluminosilicate, thermally treated perlite, calcite, diatomaceous earth or any combination of these, and is added in an amount of from 2 to 8 wt%, based on the final composition.

13. A process as claimed in any preceding claim, characterised in that the total solids present in step (i) amount to at least 60 wt% of the total composition present in step (ii).

14. A process as claimed in any preceding claim, characterised in that the total amount of free water present in steps (i), (ii) and (iii) does not exceed 8 wt%, based on the total composition.

15. A process as claimed in any preceding claim, characterised in that the temperature in the high-speed mixer/granulator is maintained below 47 °C throughout step (ii).

16. A process as claimed in any preceding claim, characterised in that the high-speed mixer/granulator is bowl-shaped and has a substantially vertical stirrer axis.

17. A process as claimed in any preceding claim, characterised in that it further comprises the step of admixing a finely divided particulate flow aid, in an amount of from 0.2 to 12.0 wt%, to the granular detergent composition or component after the granulation step (iii) is complete.

18. A process as claimed in claim 17, characterised in that the flow aid is finely divided amorphous sodium aluminosilicate, thermally treated perlite, calcite, diatomaceous earth or a combination thereof, and is added in an amount of from 0.2 to 5.0 wt%, based on the total composition.

19. A process as claimed in claim 17, characterised in that the flow aid is finely divided crystalline sodium aluminosilicate and is added in an amount of from 3.0 to 12.0 wt%, based on the total composition.

Patentansprüche

1. Verfahren zur Herstellung einer gekörnten Waschmittelzusammensetzung oder -komponente mit einer Schüttdichte von mindestens 650 g/l, wobei das verfahren den Schritt der Neutralisierung einer flüssigen sauren Vorstufe eines anionischen Tensids mit einem festen wasserlöslichen alkalischen anorganischen Material einschließt, und wobei das Verfahren gekennzeichnet ist durch die Schritte:
   (i) Aufwirbeln eines teilchenförmigen festen wasserlöslichen, alkalischen, anorganischen Materials in einer Menge im Überschuß zu jener, die für eine Neutralisation erforderlich ist, gegebenenfalls in Anmischung mit einem oder mehreren anderen teilchenförmigen Feststoffen in einem Hochgeschwindigkeitsmischer/Granulator, der sowohl eine Rührwirkung als auch Schneidwirkung aufweist;
   (ii) allmähliche Zugabe der sauren Vorstufe zu dem Hochgeschwindigkeitsmischer/Granulator unter Beibehalten einer Temperatur von nicht mehr als 55 °C, wodurch Neutralisation der sauren Vorstufe durch das wasserlösliche alkalische anorganische Material stattfindet, während das Gemisch in Teilchenform verbleibt;
   (iii) Granulieren des Gemisches in dem Hochgeschwindigkeitsmischer/Granulator in Gegenwart eines flüssigen Bindemittels,
   wodurch eine gekörnte Waschmittelzusammensetzung oder -komponente mit einer Schüttdichte von mindestens 650 g/l gebildet wird.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet**, daß das teilchenförmige, wasserlösliche, alkalische, anorganische Material Natriumcarbonat umfaßt.

3. Verfahren nach Anspruch 2, **dadurch gekennzeichnet**, daß das teilchenförmige, wasserlösliche, alkalische, anorganische Material Natriumcarbonat in Anmischung mit Natriumbicarbonat und/oder Natriumsilicat umfaßt.

4. Verfahren nach einem vorangehenden Anspruch, **dadurch gekennzeichnet**, daß die saure Vorstufe eine lineare Alkylbenzolsulfonsäure ist.

5. Verfahren nach einem vorangehenden Anspruch, **dadurch gekennzeichnet**, daß das Verhältnis von Flüssigkeiten zu Feststoffen am Ende des Schrittes (ii) nicht größer als 0,60 ist.

6. Verfahren nach einem vorangehenden Anspruch, **dadurch gekennzeichnet**, daß in Schritt (ii) die saure Vorstufe innerhalb eines Zeitraums von 2 bis 12 Minuten zugegeben wird.

7. Verfahren nach einem vorangehenden Anspruch, **dadurch gekennzeichnet**, daß Wasser vor oder zusammen mit der sauren Vorstufe in Schritt (ii) in einer Menge von 0,5 bis 2,0 Gew.-%, bezogen auf die in Schritten (i) und (ii) vorliegende Trockenmasse, zugegeben wird.

8. Verfahren nach einem vorangehenden Anspruch, **dadurch gekennzeichnet**, daß die in Schritt (i) vorliegenden Feststoffe Natriumcarbonat in Anmischung mit einem oder mehreren Waschmittelbuildern, ausgewählt aus kristallinen und amorphen Alkalimetallaluminosilicaten, Alkalimetallphosphaten und Gemischen davon, umfassen.

9. Verfahren nach einem vorangehenden Anspruch, **dadurch gekennzeichnet**, daß die in Schritt (i) vorliegenden Feststoffe zusätzlich ein Tensid in Pulverform umfassen.

10. Verfahren nach einem vorangehenden Anspruch, **dadurch gekennzeichnet**, daß die in Schritt (i) vorliegenden Feststoffe ein sprühgetrocknetes Waschmittelgrundpulver umfassen.

11. Verfahren nach einem vorangehenden Anspruch, **dadurch gekennzeichnet**, daß die während Schritt (i) vorliegenden teilchenförmigen Feststoffe eine fein verteilte teilchenförmige Fließhilfe einschließen.

12. Verfahren nach Anspruch 11, **dadurch gekennzeichnet**, daß die Fließhilfe Zeolith, amorphes Alkalimetallaluminosilicat, thermisch behandelter Perlit, Calcit, Diatomeenerde oder eine beliebige Kombination von diesen ist und in einer Menge von 2 bis 8 Gew.-%, bezogen auf die fertige Zusammensetzung, zugegeben wird.

13. Verfahren nach einem vorangehenden Anspruch, **dadurch gekennzeichnet**, daß die in Schritt (i) vorliegende Menge an gesamten Feststoffen mindestens 60 Gew.-% der in Schritt (ii) vorliegenden gesamten Zusammensetzung beträgt.

14. Verfahren nach einem vorangehenden Anspruch, **dadurch gekennzeichnet**, daß die Gesamtmengen an in den Schritten (i), (ii) und (iii) vorliegendem freiem Wasser 8 Gew.-%, bezogen auf die gesamte Zusammensetzung, nicht übersteigt.

15. Verfahren nach einem vorangehenden Anspruch, **dadurch gekennzeichnet**, daß die Temperatur in dem Hochgeschwindigkeitsmischer/Granulator unterhalb 47 °C während Schritt (ii) beibehalten wird.

16. Verfahren nach einem vorangehenden Anspruch, **dadurch gekennzeichnet**, daß der Hochgeschwindigkeitsmischer/Granulator Schalenform aufweist und eine im wesentlichen vertikale Rührerachse aufweist.

17. Verfahren nach einem vorangehenden Anspruch, **dadurch gekennzeichnet**, daß es zusätzlich den Schritt des Anmischens einer fein verteilten teilchenförmigen Fließhilfe in einer Menge von 0,2 bis 12,0 Gew.-% zu der gekörnten Waschmittelzusammensetzung oder -komponente, nachdem der Granulierungschritt (iii) beendet ist, umfaßt.

18. Verfahren nach Anspruch 17, **dadurch gekennzeichnet**, daß die Fließhilfe fein verteiltes amorphes Natriumaluminosilicat, thermisch behandelter Perlit, Calcit, Diatomeenerde oder eine Kombination davon ist und in einer Menge von 0,2 bis 5,0 Gew.-%, bezogen auf die gesamte Zusammensetzung, zugegeben wird.

19. Verfahren nach Anspruch 17, **dadurch gekennzeichnet**, daß die Fließhilfe fein verteiltes kristallines Natriumaluminosilicat ist und in einer Menge von 3,0 bis 12,0 Gew.-%, bezogen auf die gesamte Zusammensetzung, zugegeben wird.

Revendications

1. Un procédé pour la préparation d'une composition ou de composants détergents granulaires ayant une densité apparente d'au moins 650 g/litre, ce procédé comprenant l'étape de neutralisation d'un précurseur acide liquide d'un tensio-actif anionique avec un matériau inorganique alcalin solide hydrosoluble, le procédé se caractérisant par les phases suivantes :
   (i) la fluidisation d'un matériau inorganique alcalin solide hydrosoluble particulaire dans une quantité supérieure à celle nécessaire pour la neutralisation, facultativement en mélange avec un ou plusieurs autres solides particulaires, dans un mélangeur/granulateur à grande vitesse ayant à la fois une action d'agitation et de coupe ;
   (ii) l'addition progressive du précurseur acide au mélangeur/granulateur à grande vitesse, tout en maintenant une température ne dépassant pas à 55 ° C, grâce à quoi la neutralisation du précurseur acide par le matériau inorganique alcalin hydrosoluble se produit tandis que le mélange reste sous forme particulaire ;
   (iii) la granulation du mélange dans le mélangeur/granulateur à grande vitesse, en présence d'un liant liquide,

   par lequel est constitué une composition ou un composant détergent granulaire ayant une densité apparente d'au moins 650 g/litre.

2. Un procédé selon la revendication 1, caractérisé en ce que le matériau inorganique alcalin hydrosoluble particulaire comprend du carbonate de sodium.

3. Un procédé selon la revendication 2, caractérisé en ce que le matériau inorganique alcalin hydrosoluble particulaire comprend du carbonate de sodium en mélange avec du bicarbonate de sodium et/ou du silicate de sodium.

4. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le précurseur acide est un acide sulfonique d'alkylbenzène linéaire.

5. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le rapport des liquides et des solides à la fin de l'étape (ii) n'est pas supérieur à 0,60.

6. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le précurseur acide est ajouté sur une durée de 2 à 12 minutes au cours de l'étape (ii).

7. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que de l'eau est incorporée avant ou en même temps que le précurseur acide au cours de l'étape (ii), dans une quantité allant de 0,5 à 2,0 pour cent en masse sur la base du total des solides présents dans les étapes (i) et (ii).

8. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que les solides présents dans l'étape (i) comprennent du carbonate de sodium en mélange avec un ou plusieurs édificateurs de détergence choisis parmi des aluminosilicates de métaux alcalins amorphes et cristallins, des phosphates de métaux alcalins, et des mélanges de ceux-ci.

9. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que les solides présents dans l'étape (i) comprennent en outre un tensio-actif sous forme de poudre.

10. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que les solides présents dans l'étape (i) comprennent une poudre de base détergente séchée par pulvérisation.

11. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que les solides particulaires présents dans l'étape (i) comprennent un auxiliaire de fluidité particulaire finement divisé.

12. Un procédé selon la revendication 11, caractérisé en ce que l'auxiliaire de fluidité est de la zéolite, un aluminosilicate de métal alcalin amorphe, de la perlite thermotraitée, de la calcite, de la diatomite ou toute combinaison de ceux-ci, et est ajouté dans une quantité allant de 2 à 8 pour cent en masse, sur la base de la composition finale.

13. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le total des solides présents dans l'étape (i) correspond à au moins 60 pour cent en masse de la composition totale présente dans l'étape (ii).

14. Un procédé selon l'une quelconque des revendications précédentestoute revendication précédente, caractérisé en ce que la quantité totale d'eau libre présente dans les étapes (i), (ii) et (iii) ne dépasse pas 8 pour cent en masse, sur la base de la composition totale.

15. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la température dans le mélangeur/granulateur à grande vitesse est maintenue en dessous de 47° C pendant toute l'étape (ii).

16. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le mélangeur/granulateur à grande vitesse est en forme de bol et a un axe d'agitation substantiellement vertical.

17. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce qu'il comprend en outre l'étape de mélange d'un auxiliaire de fluidité particulaire finement divisé, dans une quantité allant de 0,2 à 12,0 pour cent en masse, à la composition ou au composé granulaire détergent après achèvement de l'étape de granulation (iii).

18. Un procédé selon la revendication 17, caractérisé en ce que l'auxiliaire de fluidité est de la zéolite, de l'aluminosilicate de sodium amorphe, de la perlite thermotraitée, de la calcite, de la diatomite ou toute combinaisons de ceux-ci, et est ajouté dans une quantité allant de 0,2 à 5,0 pour cent en masse, sur la base de la composition finale.

19. Un procédé selon la revendication 17, caractérisé en ce que l'auxiliaire de fluidité est de l'aluminosilicate de sodium cristallin et est ajouté dans une quantité allant de 3,0 à 12,0 pour cent en masse, sur la base de la composition finale.